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Characterization of low concentration uranium glass working materials

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Auspices Statement

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Abstract

A series of uranium-doped silicate glasses were created at (Lawrence Livermore National Laboratory) LLNL, to be used as working reference material analogs for low uranium concentration research. Specifically, the aim of this effort was the generation of well-characterized glasses spanning a range of concentrations and compositions, and of sufficient homogeneity in uranium concentration and isotopic composition, for instrumentation research and development purposes. Two base glasses were utilized and characterized to produce a total of 19 U-doped glasses, with a targeted variance in ^{235}U content from $\sim 0.725\%$ (natural uranium), $\sim 53\%$, and $\sim 94\%$, across three U concentrations from ~ 5 , ~ 50 , and ~ 500 ppm. To create these glasses, powdered base glasses were doped with uranium solutions of varying isotopic compositions, and then repeatedly melted, homogenized, and quenched. Fragments from each glass ($n = 3$ to 5 per glass) were then dissolved, chemically purified, and analyzed by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) to determine glass uranium concentration and isotopic composition, and to assess the degree of heterogeneity within the precision of the bulk chemical MC-ICP-MS technique. While the glasses are generally not homogeneous within the precision of the MC-ICP-MS technique, glasses are sufficient for use in research and development if utilized with an understanding of the limits of homogeneity. A subset of glasses is sufficiently homogeneous in uranium isotopic composition to be effectively homogeneous within the precision of most spatially-resolved techniques, but have been characterized in bulk, and not evaluated spatially at present. In all cases, the uranium-doped glasses show significantly larger variability in uranium concentration ($\sim 10\%$), however, making most of these glasses poor choices for standardization of uranium concentration measurements. While the glasses produced here are not intended to replace or become standard materials for uranium concentration or uranium isotopic composition, it is hoped that they will help fill a current gap, providing low-level uranium glasses sufficient for methods development and method comparisons within the limitations of the produced glass suite. Glasses are available for research use by request.

1. Introduction

The goal of this work was to generate a set of low concentration U-silicate test materials suitable for evaluating analytical methods where uranium isotope compositions and uranium concentrations are of interest, and applicable to real world samples such as glassy fallout (Fig. 1). In addition, it was intended to create glasses that could serve as working reference materials for methods development for *in situ* analytical methods such as resonance ionization mass spectrometry (RIMS), laser-induced breakdown spectroscopy (LIBS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and various types of secondary ion mass spectrometry (SIMS).

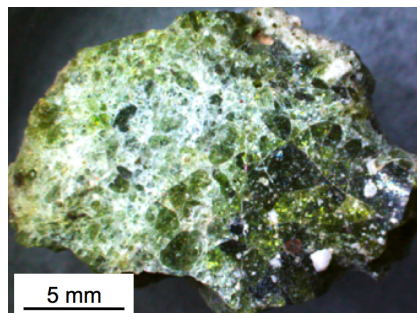


Figure 1: Glassy fallout can contain residual actinides such as U and/or Pu at part-per-million concentrations by weight.

While many analytical methods require low-concentration uranium test materials representing a range of isotopic enrichments as the basis for assessing accuracy and precision, few, if any, appropriate standards exist for these purposes (Leggit *et al.*, 2009; Inn *et al.*, 2013). Ideal working reference materials must be well-characterized for uranium concentration and isotopic composition, homogenous at a spatial level appropriate to the application, and representative of the real-world materials of interest. Among existing U-containing standard materials are the NBS 600-series of glass element standards which contain ~500, 50, 5 and 0 ppm U, and a suite of additional elements. These glasses cover a limited range of isotopic ratios (~natural), and have not been certified for use as isotopic standards. There exist U-rich oxide standards (e.g., U_3O_8) available from NBL and IRMM covering a wide range of isotopic compositions, but these are available in high U-concentrations (~85%), only. Finally, there exist a set of IRMM standard glasses (Raptis *et al.*, 2002) with a ~10 mm grain size, containing ~4 - 5 wt. % U, and created with ^{235}U enrichments of ~0%, 4% and 34%. These latter materials are glasses with a range of uranium isotope values, but their uranium concentrations are too high to be useful for most low-level uranium measurement research applications.

The glasses produced and characterized in this effort are not intended to replace or become official standard materials for uranium concentration or uranium isotopic composition. Rather, it is hoped that they will fill a current gap for low-level uranium work with glasses, enabling methods development and method comparisons within the limitations of the produced glass suite until a time when certified reference materials become widely available.

2. Production of Low-Concentration Uranium Glasses

A total of five batches were created in the effort to produce relatively homogeneous glasses in a series of uranium concentrations (~5, ~50, and ~500 ppm) and isotopic compositions (~natural, ~53 %, and ~94 %). The uranium concentrations and isotopic compositions chosen for the glasses were selected to cover a range relevant to general nuclear material analysis. The starting glass matrix composition was selected to be similar to the major element composition of typical historical fallout melt glass from United States nuclear weapons tests (e.g., Eppich *et al.*, 2014, Lewis *et al.*, 2015), and was selected to coincide with the CAS-3 eutectic composition in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system (Osborn & Muan, 1960): 62.0% SiO_2 , 14.5% Al_2O_3 , 23.5% CaO (see Fig. 2, CAS-3). The high SiO_2 and Al_2O_3 concentrations of this eutectic reflect the composition observed in fallout glasses. CaO content has been observed to vary over an order of magnitude in

some fallout melt glass sample suites (Eppich *et al.*, 2014), and thus was not considered to be of first-order importance.

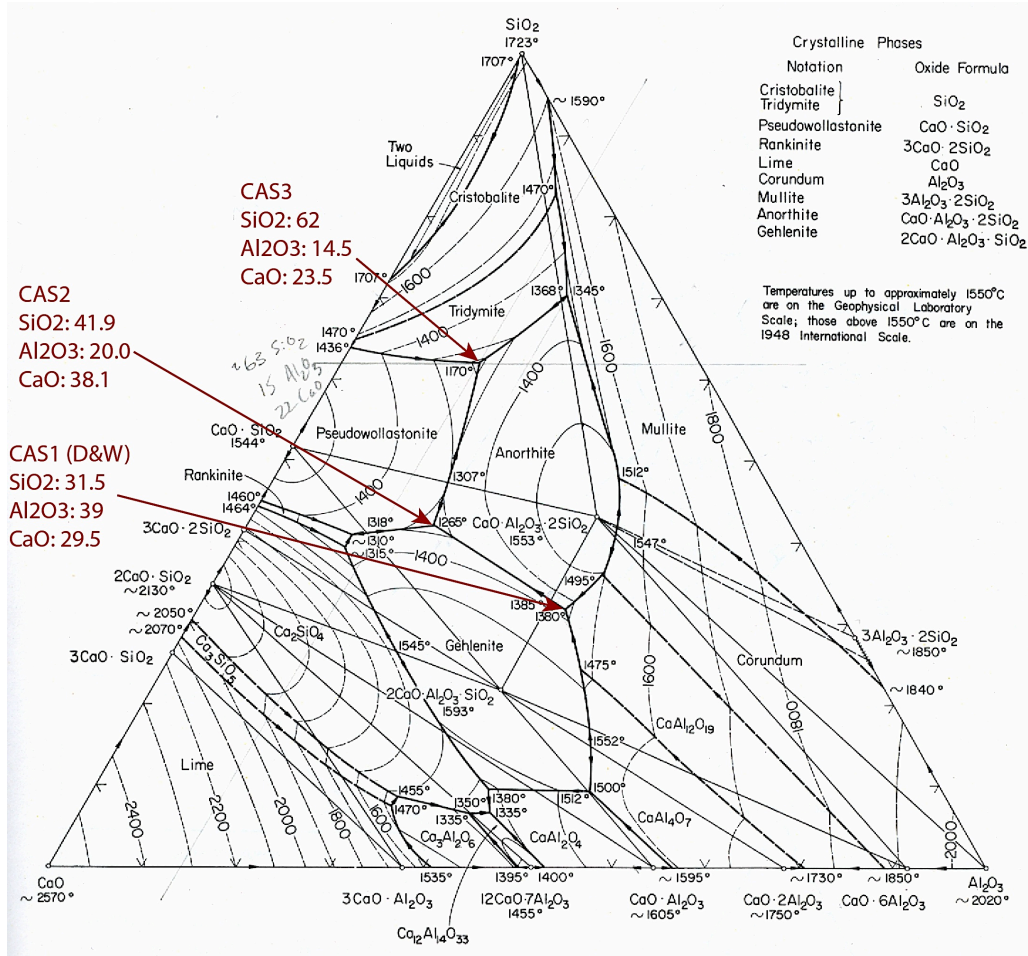


Figure 2: The CaO-Al₂O₃-SiO₂ system from Osborn and Munn, 1960, with several potential eutectics highlighted. The final base glass composition chosen was that of CAS3.

To generate the starting (base) glass composition used for all U-doped glasses, pure SiO₂, Al₂O₃, and CaCO₃ were ground together using an agate mortar and pestle for ~60 minutes with ethanol. The mixture was calcined at 850 °C overnight in a Deltech DT-31 bottom-loading furnace (Fig. 3) to decompose the CaCO₃, then re-ground in an agate mortar and pestle for another 60 minutes with ethanol (Fig. 3). The mixture was then fused at 1450 °C in a Pt-Au crucible in air for 8 hours before quenching in water. The resultant glass was crushed in two steps. First, the glass was crushed to mm-sized pieces using a steel mortar and pestle. Next, the glass chips were ground in an agate mortar and pestle for ~60 minutes with ethanol. The powder was then re-fused at 1450 °C in a Pt crucible and reground and fused two additional times, for a total of three fuse/grind cycles. Approximately 150 g of final product base glass powder was generated, and is called the ‘CAS glass’ in this report. A second base glass of the same composition, called the ‘SAC glass’ in this report, was purchased directly from Specialty Glass, Inc., to minimize non-natural U contamination contributions from initial fusing steps done in house.



Fig. 3: From left to right: Powdered glass slurry in an agate mortar; A Pt crucible being heated in the furnace; Quenched glass in the Pt crucible.

Three uranium solutions, with isotopic compositions of ~natural, ~53% ^{235}U , and ~94% ^{235}U (isotopic compositions of dopant solutions are presented in Table 1), and prepared in nitric acid, were selected to dope ~10 g batches of finely-ground base glass. The ~94% solution was prepared from a New Brunswick Laboratories Nuclear Forensic Reference Material (NFRM U-1), a uranium oxide powder. The ~53% solution was similarly prepared from NFRM U-2, also a uranium oxide powder. Values for these two materials are noted in Table 1, but currently these certificates remain in draft form. The ~natural solution was prepared from a Certified Reference Material, the CRM 112-A solution. Prepared solutions were added as nitrate solutions to the powdered base glasses, and ground under ethanol. The slurry was then fused in a 25 mL Pt crucible at 1450 °C and finely ground in an agate mortar and pestle. Fusing times varied by sample, with most samples undergoing three fusion/grinding cycles. The final product was several grams of glass shard of each composition, as broken from the crucible after the final fuse.

Table 1: Target concentrations of new U glasses, and the reported isotopic compositions of the solutions used to dope the base glasses. Ratios are given as atom ratios, target concentrations are provided by weight. Uncertainties are expressed as expanded uncertainties ($k = 2$).

glass	U (ppm)	dopant	$^{234}\text{U} / ^{238}\text{U}$	uncert.	$^{235}\text{U} / ^{238}\text{U}$	uncert.	$^{236}\text{U} / ^{238}\text{U}$	uncert.
Natural	5, 50, 500	CRM 112-A	0.000052841	0.000000082	0.0072543	0.0000040	<i>n.d.</i>	
~53% ^{235}U	5, 50, 500	NFRM U-2	0.008067	0.000028	1.1340	0.0020	0.005691	0.000013
~94% ^{235}U	5, 50, 500	NFRM U-1	0.17942	0.00058	16.984	0.017	0.05332	0.00038

From a total of two base glasses ('CAS' and 'SAC'), a set of 19 uranium doped glasses were produced by this study through five separate batches of glass production. Batches 1 and 2 produced three and nine uranium doped glasses, respectively, while seven additional glasses were produced in Batches 3, 4 and 5.

Table 2: Summary of glass standard preparation steps employed in each sample batch. Batch 3, 4, and 5 were re-homogenized from the doped end-products of Batch 1 and 2 in order to produce a more homogeneous series of glasses.

batch	doped glasses	base glass	re-homogenized?
1	3	CAS	No
2	9	SAC	No
3	1	SAC	Yes, from Batch 2
4	3	CAS	Yes, from Batch 1
5	3	SAC	Yes, from Batch 2

In later batches (Batch 3, 4, and 5), doped glasses produced by the methods above were reprocessed in order to produce more homogeneous end-products. To do this, select glasses were re-crushed, re-melted, and quenched several additional times. A summary of the glass preparation steps for each batch is provided in Table 2. Batch 3 produced a single refused glass to verify results, and Batches 4 and 5 produced three glasses, each.

3. Uranium Concentration and Isotope Ratio Measurement Methods

3a. Analytical Methods

Individual pieces (0.05-0.5 g total mass) of each of the 21 produced glasses were washed using 18.2 MΩ H₂O, dried, and weighed to a precision of 0.0001 g using a standard laboratory balance (Mettler Toledo). Samples were then placed in clean Teflon beakers for dissolution. An approximately 2:1 mixture of HNO₃ to HF was added to each beaker, the beakers were capped, then heated for ~24 hours. All acids used in this study were “ultra-trace” grade (Seastar BASELINE, Seastar Chemicals, Inc.), with U concentrations < 0.05 pg/g. Acids were diluted using 18.2 MΩ H₂O. After heating, beakers were uncapped, and ~1 mL of concentrated HClO₄ was added to each beaker in order to dissolve the fluoride compounds that precipitated. Samples were then dried down, dissolved in 1 mL concentrated HCl, and dried down again. Finally, samples were dissolved in ~5 mL 3 M HCl. Using this treatment, all samples were completely dissolved, with no residual solid fraction remaining. Masses were obtained for the 3 M HCl solutions (hereafter referred to as “stock solutions”).

Uranium concentrations and isotopic compositions were measured in chemically-purified aliquots of stock solutions using multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS). Uranium concentrations were obtained following the principles of isotope dilution mass spectrometry (IDMS). Separate aliquots of stock solutions were used for the uranium concentration and uranium isotopic composition measurements. Sample aliquots used for uranium concentration measurements were spiked with an internally-calibrated ²³³U spike. Sample aliquots used for uranium isotopic composition measurements were unspiked. Spiked aliquots of stock solutions were equilibrated by heating on a hot plate, capped, for ~24 hours. Both spiked and unspiked aliquots followed the same procedure after this point. Aliquots were dried down and dissolved twice in 100 μL concentrated HNO₃.

After the second HNO₃ dissolution, the precipitates were dissolved in 1 mL 4 M HNO₃ for the first of two ion chromatography uranium separation steps. Poly-Prep columns with 1.8 mL resin reservoirs (Bio-Rad Laboratories) were loaded with 1.8 mL U-TEVA ion exchange resin (Eichrom Technologies) and conditioned with 10 mL 4 M HNO₃. Samples were loaded onto the resin, and the resin was washed with 5 mL 4 M HNO₃, 3 mL 9 M HCl, and 4 mL 5 M HCl to remove matrix elements, while U remained sorbed to the resin. Uranium was eluted by adding 8 mL 0.1 M HCl. Eluates containing U were dried down and dissolved in 100 μL concentrated HCl twice, then dried down a third time.

For the final U purification step, the precipitates from the previous step were dissolved in 1 mL 9 M HCl. Poly-Prep columns were loaded with 1.8 mL AG-1 X8 (100-200 mesh) anion exchange resin (Bio-Rad Laboratories) and conditioned with 10 mL 9 M HCl. Samples were loaded onto the resin, and the resin was washed with 7 mL 9 M HCl to remove matrix elements, while U remained sorbed to the resin. Uranium was then eluted from the resin by adding 8 mL 0.1 M HCl.

Eluates containing U were dried down and dissolved twice in concentrated HNO₃, dried down a third time, and dissolved in 3 mL 2 % HNO₃ for mass spectrometry analysis.

Samples were measured using a Nu Plasma MC-ICP-MS at LLNL. For the spiked aliquots, a routine was chosen such that ²³⁸U, ²³⁵U, and ²³³U were all measured on Faraday detectors. The choice of analytical routine for the unspiked aliquots depended upon the concentration of the minor isotopes (²³⁴U and ²³⁶U) relative to the major isotopes (²³⁵U and ²³⁸U). Generally, for the samples with isotopic compositions similar to natural uranium, a static routine was used for Nu Plasma analyses, with ²³⁸U and ²³⁵U measured on Faraday detectors, and ²³⁶U and ²³⁴U measured on ion counters.

Mass bias correction factors (MBCFs) were calculated using the measured and certified ²³⁸U/²³⁵U ratio of the natural uranium isotopic standards CRM 112-A and/or CRM U100, and these corrections were applied to all subsequent analyses. The CRM 112-A standard was run 3-5 times throughout the course of a run, and the average calculated MBCF was applied to each unknown. The Faraday-ion counter detector gain factors (DGFs) were also determined in the same analytical routine as the MBCF by measuring CRM 112-A with ²³⁵U and ²³⁸U measured on Faraday detectors and ²³³U, ²³⁴U, and ²³⁶U measured on the three ion counters. The isotope ratio measurements for determining DGFs were corrected using the calculated MBCF for ²³⁸U/²³⁵U. The measured DGFs and calculated MBCFs were applied to subsequent sample analyses. Spiked samples were corrected for the addition of ²³⁵U and ²³⁸U from the impure spike by subtracting the contribution of each isotope using the measured intensity of ²³³U and the known ratio of each U isotope in the spike with respect to ²³³U. This was a relatively minor correction, compared to the correction for mass bias and Faraday-ion counter gain factor.

In order to assess measurement accuracy, at least one uranium isotopic standard was analyzed alongside unknowns as a quality control standard. Typically, we employed CRM U005-A. Our results generally show excellent agreement with the certified isotopic values of U005-A, giving us high confidence in the accuracy of the measurements, as well as the calculations performed in order to obtain the measured isotope ratios for unknowns.

All calculations of uncertainty for uranium measurements described below are performed following the guidance of Working Group 1 of the Joint Committee for Guides in Metrology as described in the document *Evaluation of measurement data – Guide to the expression of uncertainty in measurement* (JGCM 100 : 2008). Uranium concentrations and isotopic compositions are reported as a combined standard uncertainty with a coverage factor of k = 2.

3b. Quality Control Measurements

Several steps were taken in order to assess confidence in measurements and assessment of sample-to-sample heterogeneity. Total procedural blanks were performed with each measurement batch. The total procedural blanks prepared in this study received the same reagents, underwent the same chemical separation procedures, and were analyzed using identical methods as the samples. Therefore, the procedural blanks can be used to assess whether, and to what degree, the samples are contaminated by uranium present in the laboratory workspace. In all cases, the results of total procedural blanks demonstrated that sample contamination of uranium in the laboratory is negligible, and can be ignored. Typical total procedural blanks contain less than 10 pg total uranium. In all cases, only ²³⁸U was detected; the other uranium isotopes were present in blanks at concentrations below the detection limit of the MC-ICP-MS.

Total procedural replicates of individual solutions were performed to confirm our findings regarding negligible laboratory blank. In this procedure, two aliquots of an individually dissolved piece of a specific glass standard were subjected to identical chemical separation techniques, and analyzed concurrently. If laboratory blank is negligible, the measured isotopic composition of the replicate sample aliquots should overlap within uncertainty of each other. We present the results of these analyses for three such solutions in Table 3. In all cases, the measured $^{235}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$ ratios overlap within uncertainty. These results give us high confidence in the accuracy and precision in subsequent measurements, presented below.

Table 3: Results of procedural duplicates of three samples prepared for this study (k=2).

Sample ID	$^{235}\text{U} / ^{238}\text{U}$ (atom ratio)	uncert.	$^{234}\text{U} / ^{238}\text{U}$ (atom ratio)	uncert.	$^{236}\text{U} / ^{238}\text{U}$ (atom ratio)	uncert.
<i>Duplicate Set #1</i>						
LLNL-U1-50 (1)	0.007442	0.000004	0.00005464	0.00000013	0.000000596	0.000000015
LLNL-U1-50 (1) DUP	0.007436	0.000004	0.00005452	0.00000013	0.000000573	0.000000014
<i>Duplicate Set #2</i>						
LLNL-U1-500 (2)	0.007259	0.000004	0.00005280	0.00000012	0.000000085	0.000000015
LLNL-U1-500 (2) DUP	0.007263	0.000004	0.00005277	0.00000012	0.000000083	0.000000016
<i>Duplicate Set #3</i>						
LLNL-U1-500 (3)	0.007260	0.000004	0.00005287	0.00000012	0.000000070	0.000000015
LLNL-U1-500 (3) DUP	0.007262	0.000004	0.00005288	0.00000012	0.000000071	0.000000014

4. Characterization of Low-Concentration Uranium Glasses

Results of uranium concentration and uranium isotopic composition analyses are described below, and a summary of all measured results, including calculation of variance of uranium concentration, $^{235}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$, are presented in Table 4. We then discuss each produced glass in terms of the batch in which it was produced, with full data for each batch in Table 5 through Table 9. We show that while contamination of the glasses from sources other than the dopant solution was fairly ubiquitous, evolution of the manufacturing process led to improved glass homogeneity in subsequent batches. For each glass produced in Batches 3, 4, and 5, plots of individual analytical data with uncertainties are provided in the text. While produced glasses did not result in achieving the targeted uranium concentrations (5, 50, 500 ppm U), and the targeted isotopic compositions (natural, ~53%, and ~94% ^{235}U enriched), and we refer to them as such for consistency in the text.

Table 4: Summarized uranium concentration and isotopic composition measurements from 2 base glasses (CAS and SAC), and 19 U-doped glasses. Individual results are presented in Tables 5-9. RSD% is the 1 σ relative percent standard deviation of the replicate analyses (measuring different shards from a given glass sample) relative to the mean value for each parameter.

Sample ID	(n =)	U ($\mu\text{g/g}$)	RSD %	$^{235}\text{U} / ^{238}\text{U}$	RSD %	$^{234}\text{U} / ^{238}\text{U}$	RSD %	$^{236}\text{U} / ^{238}\text{U}$	RSD %
<i>Batch 1</i>									
B1-CAS-Base	3	0.41	4.38	0.1232	40.78	0.001252	41.97	0.00037074	43.79
B1-CAS-Nat-5	3	5.03	2.69	0.0084	1.28	0.000063	1.61	0.00000383	10.40
B1-CAS-Nat-50	3	37.57	0.34	0.0074	0.15	0.000054	0.37	0.00000057	4.89
B1-CAS-Nat-500	3	366.67	11.88	0.0073	0.02	0.000053	0.16	0.00000009	19.92

Sample ID	(n =)	U (µg/g)	RSD %	²³⁵ U / ²³⁸ U	RSD %	²³⁴ U / ²³⁸ U	RSD %	²³⁶ U / ²³⁸ U	RSD %
Batch 2									
B2-SAC-Base	5	0.31	0.84	0.0072	0.13	0.000054	0.11	-	
B2-SAC-Nat-5	3	5.328	1.25	0.0208	0.73	0.000188	0.86	-	
B2-SAC-Nat-50	3	48.82	0.36	0.0202	1.06	0.000185	1.03	-	
B2-SAC-Nat-500	3	423.73	8.12	0.0082	0.19	0.000062	0.35	-	
B2-SAC-53-5	3	5.31	1.52	0.9228	0.09	0.006588	0.14	-	
B2-SAC-53-50	3	44.67	2.26	1.0992	0.11	0.007831	0.16	-	
B2-SAC-53-500	3	464.37	9.49	1.1270	0.02	0.008007	0.08	-	
B2-SAC-94-5	3	4.77	12.75	6.1517	4.57	0.064885	4.67	-	
B2-SAC-94-50	3	43.23	8.13	6.4553	0.37	0.068147	0.57	-	
B2-SAC-94-500	3	409.33	6.84	15.9180	0.78	0.168171	0.77	-	
Batch 3									
B3-SAC-Nat-500	5	257.63	4.88	0.0082	0.05	0.000062	0.18	0.00000332	0.70
Batch 4									
B4-CAS-Nat-500	3	373.63	2.04	0.0080	0.24	0.000060	0.07	0.00000253	5.75
B4-CAS-53-500	3	331.47	2.65	1.1253	0.02	0.010622	0.02	0.00777333	0.05
B4-CAS-94-500	3	336.47	4.24	16.0367	0.14	0.225077	0.14	0.06985333	0.14
Batch 5									
B5-SAC-53-5	3	4.34		0.9191	0.39	0.006554	0.38	0.00458201	0.52
B5-SAC-53-50	3	41.88	7.27	1.0984	0.15	0.007806	0.17	0.00549771	0.12
B5-SAC-53-500	3	413.25	5.17	1.1283	0.06	0.008017	0.08	0.00564667	0.05

4a. Batch 1 Glasses

The Batch 1 glasses are a suite of three glasses doped with CRM 112-A (of ~natural isotopic composition) in varying uranium concentrations (~5 ppm, ~50 ppm, and ~500 ppm). Also included in this batch is characterization of the ‘CAS’ base glass used for the subsequent manufacture of the three CRM 112-A doped glasses. Three individual pieces of from each produced glass, including the CAS base glass, were analyzed (Table 5).

Table 5: Uranium concentrations and isotopic compositions of Batch 1 glass measurements. Isotope ratios are expressed as atom ratios, the standard uncertainty is given for (k=2).

Sample ID	U (µg/g)	uncert.	²³⁵ U / ²³⁸ U	uncert.	²³⁴ U / ²³⁸ U	uncert.	²³⁶ U / ²³⁸ U	uncert.
<i>Base glass</i>								
CAS (1)	0.4193	0.0011	0.14464	0.00008	0.001482	0.000003	0.0004424	0.0000018
CAS (2)	0.4168	0.0008	0.15919	0.00008	0.001622	0.000004	0.000485	0.000002
CAS (3)	0.3872	0.0015	0.06580	0.00004	0.0006506	0.0000016	0.0001849	0.0000008
<i>CRM 112-A doped glass</i>								
<i>~5 ppm</i>								
CAS-Nat-5 (1)	5.179	0.012	0.008268	0.000004	0.00006219	0.00000015	0.00000428	0.00000003
CAS-Nat-5 (2)	4.988	0.012	0.008413	0.000004	0.00006347	0.00000015	0.00000356	0.00000002
CAS-Nat-5 (3)	4.918	0.011	0.008479	0.000004	0.00006420	0.00000015	0.00000364	0.00000002
<i>~50 ppm</i>								
CAS-Nat-50 (1)	37.62	0.08	0.007442	0.000004	0.00005464	0.00000013	0.000000596	0.000000015
CAS-Nat-50 (2)	37.67	0.08	0.007422	0.000004	0.00005426	0.00000013	0.000000541	0.000000015
CAS-Nat-50 (3)	37.43	0.08	0.007440	0.000004	0.00005457	0.00000013	0.000000579	0.000000016
<i>~500 ppm</i>								
CAS-Nat-500 (1)	316.4	0.8	0.007262	0.000004	0.00005297	0.00000012	0.000000104	0.000000015
CAS-Nat-500 (2)	390.7	1.0	0.007259	0.000004	0.00005280	0.00000012	0.000000085	0.000000015
CAS-Nat-500 (3)	392.9	1.0	0.007260	0.000004	0.00005287	0.00000012	0.000000070	0.000000015

The CAS base glass was characterized to assess the uranium concentration and isotopic composition of the material used for manufacture of some of the uranium doped glasses. The measured uranium isotopic composition of the CAS base glass, made from initially pure starting reagents prior to a fusing-crushing cycle, would be expected to have a negligible uranium concentration with an isotopic composition near natural. Instead, the base glass was found to contain a non-negligible concentration of uranium, with the uranium concentration in the three measurements of the base glass varying well outside of uncertainty, from 0.3872 to 0.4193 $\mu\text{g/g}$. Isotopic measurements reflect a non-natural uranium isotopic composition, with enrichment in all measured light uranium isotopes. Furthermore, we found that this non-natural uranium is not homogeneously distributed in the base glass. The isotopic composition of the three measurements varies significantly, well outside of uncertainty. The $^{235}\text{U}/^{238}\text{U}$ ratio varies by greater than a factor of two, from 0.06580 to 0.15919, and the $^{234}\text{U}/^{238}\text{U}$ ratio varies from 0.0006506 to 0.001622. In addition, the base glass samples contain a measurable concentration of ^{236}U , a non-naturally occurring isotope of uranium. The $^{236}\text{U}/^{238}\text{U}$ ratio of the three CAS base glass measurements varies from 0.0001849 to 0.000485. Data from three shards of CAS base glass plot along a two-component mixing line between natural uranium composition and a relatively ^{234}U , ^{235}U , and ^{236}U -enriched contaminant end-member (Fig. 4).

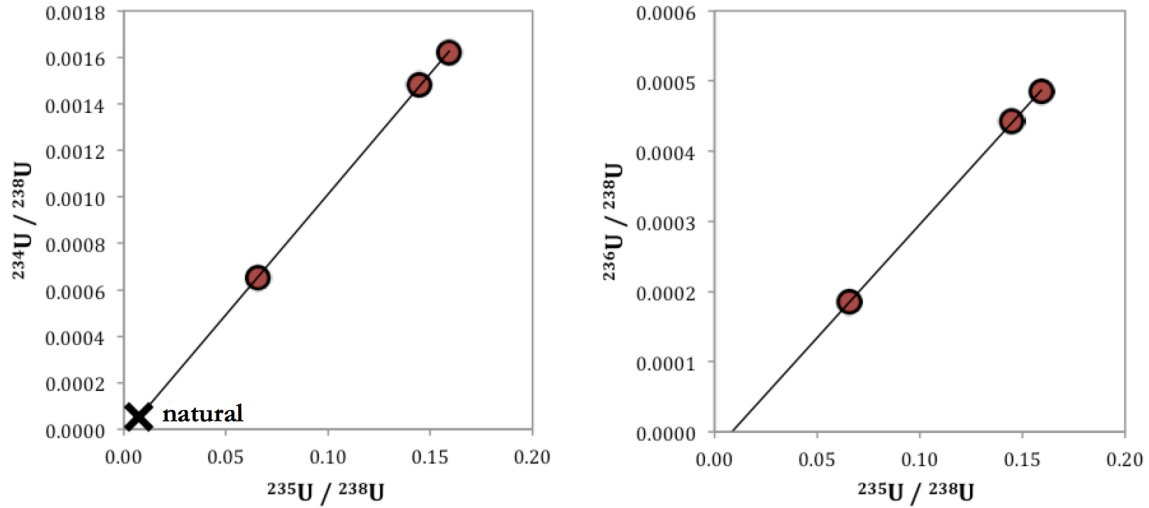


Figure 4: Measurements from three shards of the CAS base glass used for Batch 1 glass production demonstrate the effect of contamination during production. Each measurement (red circles) should plot within uncertainty of natural uranium (X on left panel), with negligible contributions from ^{236}U (right panel). Instead, all three measurements plot along a linear trend indicative of two-component mixing between natural uranium and uranium with ^{234}U , ^{235}U , and ^{236}U -enriched isotopic composition. This contribution of contamination during the crushing and fusing of the base glass explains, in part, both the deviation from dopant isotopic compositions, as well as the relative lack of heterogeneity of measurements produced using these methods.

The uranium heterogeneity and non-natural isotopic composition observed in the base glass shards cannot be explained by laboratory environmental contamination or sample cross-contamination during the chemical separation and analytical techniques used to obtain these data. Total procedural blanks performed alongside samples during chemical separation typically yield very low uranium concentrations, with only ^{238}U detected. Procedural duplicates were within uncertainty for uranium concentration and isotopic composition relative to the initial analyses. The significant deviation in composition from the expected values may, however, be explained as

contamination during the production process of the base glass, which was made from initially pure starting reagents, prior to a fusing-crushing cycle.

Analyses of the set of glasses produced from this CAS base glass and doped with varying concentrations of CRM 112-A show an inverse relationship between uranium concentration and deviation from the isotopic composition from the dopant (see Table 5). The base glass samples (which would have contained little to no initial uranium) are the most different in uranium isotopic composition from the dopant, while the ~5 ppm and ~50 ppm uranium doped glasses are increasingly more similar to the dopant in isotopic composition. The ~500 ppm uranium doped glass overlaps within uncertainty with the dopant composition, although this glass still contained a measurable concentration of ^{236}U ($^{236}\text{U}/^{238}\text{U}$ varying from 6.95×10^{-8} to 1.04×10^{-7}), which is absent in CRM 112-A. This suggests that the contamination present in this highest concentration sample batch was nearly completely diluted by the magnitude of added dopant. These observations are consistent with an explanation involving contamination from a single, enriched-uranium contaminant source. We conclude that batch 1 glasses were affected by a single primary contaminant, with a non-natural isotopic composition enriched in the minor uranium isotopes (^{234}U , ^{235}U , and ^{236}U), which contaminated the CAS base glass at the time of initial production.

Upon investigation, it was found that the furnace used for fusing the initial CAS base glass had a prior history of use with enriched uranium materials, and is likely the source of contamination. As the glass fused, it is likely that contaminant uranium in the furnace entered the glasses while molten. As the glass was not sufficiently mixed while molten, the contaminant uranium was not homogeneously distributed in the glass. This would explain the significant heterogeneity observed in the base glass. The doped glasses are less heterogeneous, as the increasing amount of uranium dopant added to each glass resulted in increasing dilution of the contaminant uranium. While obtaining glasses with a highly specified uranium isotopic composition and uranium concentration was not the primary aim of this study, generation of well-characterized glasses of sufficient homogeneity in uranium concentration and isotopic composition was a priority. Thus, subsequent glass production efforts attempted to minimize this effect.

The CRM 112-A doped glasses (B1-CAS-Nat-5, B1-CAS-Nat-50, and B1-CAS-Nat-500) are generally variable in uranium concentration and isotopic composition, although isotopic heterogeneity decreases with increasing uranium concentration. Although none of the glasses are homogeneous in terms of isotopic composition, we observe a dilution effect, where the increasingly higher uranium concentrations used to dope the glasses, dilute the enriched uranium contaminant originating from the furnace. The B1-CAS-Nat-50 and B1-CAS-Nat-500 glass standards are more homogeneous in terms of isotopic composition than to the CAS base glass and ~5 ppm uranium B1-CAS-Nat-5 glass. The heterogeneity observed in the ~50 ppm and ~500 ppm glasses is smaller than the precision of many spatially-resolved analytical techniques, suggesting that these glasses could be useful to research and development efforts needing to utilized a range of isotopic compositions at these uranium concentrations (~50 and ~500 ppm U).

4b. Batch 2 Glasses

Glass standards from Batch 2 were manufactured using adapted procedures to minimize contamination from the furnace, primarily by keeping the glass material covered in the furnace as much as possible and by utilizing a base glass (SAC), identical in composition to the CAS glass but produced in an environment with no prior history of uranium work. Nine uranium-doped glasses were produced at three targeted uranium concentration levels (~5 ppm, ~50 ppm, and ~500 ppm), and three targeted uranium isotopic compositions (~natural, ~53 % ^{235}U , and ~94 %

^{235}U). Characterization of the SAC base glass is also provided and discussed, here. Within this batch, five aliquots of the powdered SAC base glass were analyzed, in order to re-assess the impact of furnace contamination evident in Batch 1 glasses. Three shards of from each of the nine uranium-doped glasses were also analyzed. Uranium concentration and isotopic composition results for Batch 2 glasses are given in Table 6.

Table 6: Uranium concentrations and isotopic compositions of Batch 2 glass measurements. Isotope ratios are expressed as atom ratios, the standard uncertainty is given for (k=2). ^{236}U was not measured.

Sample ID	U ($\mu\text{g/g}$)	uncert.	$^{235}\text{U} / ^{238}\text{U}$	uncert.	$^{234}\text{U} / ^{238}\text{U}$	uncert.
<i>Base glass</i>						
SAC (1)	0.3121	0.0006	0.007232	0.000019	0.0000536	0.0000002
SAC (2)	0.3119	0.0009	0.007213	0.000019	0.0000537	0.0000002
SAC (3)	0.3096	0.0006	0.007231	0.000018	0.0000537	0.0000002
SAC (4)	0.3113	0.0009	0.007216	0.000018	0.0000536	0.0000002
SAC (5)	0.3167	0.0007	0.00723	0.00002	0.0000536	0.0000002
<i>CRM 112-A doped glass</i>						
<i>~5 ppm</i>						
SAC-Nat-5 (1)	5.252	0.009	0.020930	0.000011	0.00018936	0.00000013
SAC-Nat-5 (2)	5.355	0.007	0.020651	0.000011	0.00018618	0.00000013
SAC-Nat-5 (3)	5.376	0.006	0.020894	0.000011	0.00018833	0.00000013
<i>~50 ppm</i>						
SAC-Nat-50 (1)	48.86	0.05	0.019948	0.000010	0.00018262	0.00000012
SAC-Nat-50 (2)	48.98	0.05	0.020353	0.000010	0.00018626	0.00000012
SAC-Nat-50 (3)	48.63	0.05	0.020270	0.000010	0.00018545	0.00000012
<i>~500 ppm</i>						
SAC-Nat-500 (1)	409.4	0.5	0.008173	0.000004	0.00006185	0.00000004
SAC-Nat-500 (2)	398.8	0.5	0.008145	0.000004	0.00006143	0.00000004
SAC-Nat-500 (3)	463.0	0.6	0.008147	0.000004	0.00006170	0.00000004
<i>NFRM U-2 doped glass</i>						
<i>~5 ppm</i>						
SAC-53-5 (1)	5.40	0.02	0.9237	0.0005	0.006598	0.000004
SAC-53-5 (2)	5.24	0.02	0.9221	0.0005	0.006583	0.000004
SAC-53-5 (3)	5.298	0.017	0.9226	0.0005	0.006583	0.000004
<i>~50 ppm</i>						
SAC-53-50 (1)	44.20	0.13	1.0997	0.0006	0.007844	0.000004
SAC-53-50 (2)	45.83	0.16	1.1000	0.0006	0.007831	0.000004
SAC-53-50 (3)	43.98	0.19	1.0978	0.0006	0.007819	0.000004
<i>~500 ppm</i>						
SAC-53-500 (1)	512	4	1.1273	0.0006	0.008015	0.000005
SAC-53-500 (2)	456	4	1.1268	0.0006	0.008005	0.000004
SAC-53-500 (3)	425.1	1.8	1.1270	0.0006	0.008002	0.000004
<i>NFRM U-1 doped glass</i>						
<i>~5 ppm</i>						
SAC-94-5 (1)	4.88	0.03	6.119	0.004	0.06458	0.00005
SAC-94-5 (2)	4.11	0.03	5.888	0.004	0.06202	0.00005
SAC-94-5 (3)	5.31	0.03	6.448	0.004	0.06806	0.00005
<i>~50 ppm</i>						
SAC-94-50 (1)	44.0	0.3	6.482	0.004	0.06853	0.00005
SAC-94-50 (2)	39.4	0.2	6.449	0.004	0.06816	0.00005
SAC-94-50 (3)	46.3	0.3	6.435	0.004	0.06776	0.00005
<i>~500 ppm</i>						
SAC-94-500 (1)	410	3	15.994	0.011	0.16889	0.00012
SAC-94-500 (2)	437	3	15.774	0.010	0.16668	0.00012
SAC-94-500 (3)	381	3	15.986	0.012	0.16894	0.00012

Generally, results indicate that, while the glasses are still heterogeneous in terms of both uranium concentration and isotopic composition relative to the precision of the MC-ICP-MS technique,

the glasses are more homogeneous than those produced in Batch 1. Therefore, the improvements to the technique were successful in allowing for the creation of more homogeneous glasses. Of note, however, ^{236}U was not measured in this sample batch.

Results from measurement of five aliquots of the powdered ‘SAC’ base glass overlap within uncertainty in U isotopic composition (average $^{238}\text{U}/^{235}\text{U} = 138.4$; average $^{234}\text{U}/^{235}\text{U} = 0.007422$), but not U concentration. The SAC base glass isotopic composition is slightly depleted with respect to natural uranium ($^{238}\text{U}/^{235}\text{U} = 137.88$). As the base glass is a powdered glass, not a fused glass, it is difficult to assess whether the measured U concentrations and isotopic compositions are indicative of structurally-bound U, or a U contaminant sorbed to the surfaces of the powder grains. Measured U concentrations of the five SAC base glass samples are low (~ 0.3 ppm U), but show some variation outside of errors, suggesting that the trace U is not evenly distributed throughout the powder.

Measurements of three shards from each of the three concentration levels of the U-Nat glasses all show variation outside of uncertainty of each other in U concentration and in isotopic composition, indicating that these glasses are not homogeneous within the precision of the MC-ICP-MS technique. The average values measured (Table 3) in these three concentration level create a linear trend, with the \sim natural uranium dopant CRM 112-A as one end-member, and the highest uranium concentration (423 ppm U, averaged value) glasses most similar to, but not equal to, the dopant in $^{238}\text{U}/^{235}\text{U}$ and $^{234}\text{U}/^{235}\text{U}$ (Fig. 4A). The ~ 5 and ~ 50 ppm glasses are considerably different from the dopant U isotopic composition, indicating the contribution of a relatively ^{235}U and ^{234}U -enriched contaminant. This contaminant appears to be from a single source, but was not homogeneously mixed into the glasses during the manufacturing process.

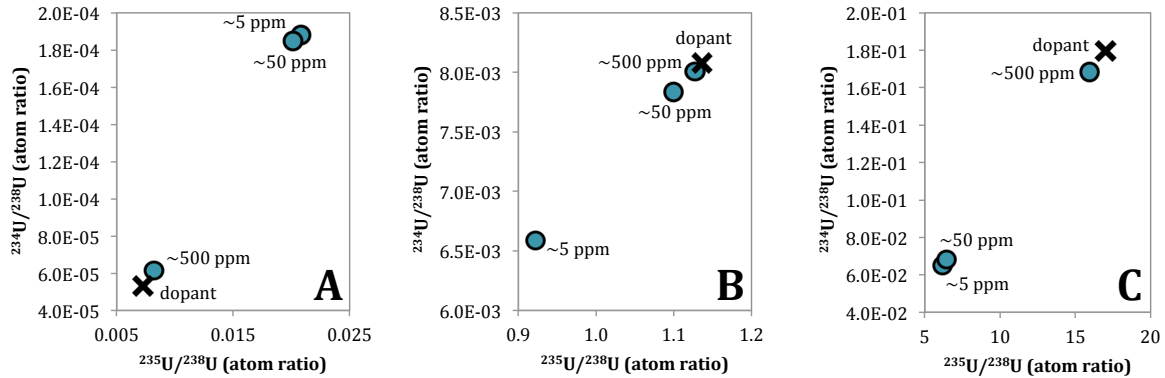


Figure 4: Average uranium isotopic compositions from Batch 2 uranium doped glasses. Blue circles, glasses; X, dopant (for A, CRM 112-A; for B, NFRM U-2; for C, NFRM U-3). Results indicate that a uranium contaminant with a $^{235}\text{U}/^{238}\text{U}$ ratio higher than the \sim natural CRM 112-A uranium dopant, but lower than the $\sim 53\%$ ^{235}U -enriched NFRM U-2 dopant mixed into the glasses during production.

The high correlation between these three isotope ratios ($R^2 > 0.99$) allows us to assume two-component mixing between dopant uranium and contaminant uranium. Under this assumption, it is possible to calculate the isotopic composition of the end-member contaminant, because of the significant spread in the $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$ between the three sets of U-doped glasses and the SAC base glass. We calculated the $^{234}\text{U}/^{235}\text{U}$ ratio of the contaminant uranium to be $\approx 1.04 \times 10^{-2}$ from the slope of a plot of $^{235}\text{U}/^{238}\text{U}$ versus $^{234}\text{U}/^{238}\text{U}$. We also calculated the $^{236}\text{U}/^{235}\text{U}$ ratio to be $\approx 3.23 \times 10^{-3}$ from the slope of a plot of $^{235}\text{U}/^{238}\text{U}$ versus $^{236}\text{U}/^{238}\text{U}$. This

uranium isotopic composition is likely characteristic of the contamination present in the furnace used to produce the glasses, and likely affected the later batches of glasses. We will address this possibility further, below.

Measurements of three shards of glass each from the three concentrations levels of the ~53% ^{235}U -enriched (doped with NFRM U-2) glasses are also outside of uncertainty of each other in U concentration and isotopic composition, and thus not homogeneous within the precision of MC-ICP-MS. Similarly to the CRM 112-A doped glasses, the most concentrated NFRM U-2 doped glass is most similar in isotopic composition to the dopant, relative to the less concentrated glasses (Fig. 4B). The lowest concentration glass does overlap with the dopant in $^{234}\text{U}/^{238}\text{U}$, though none overlap with the dopant in $^{235}\text{U}/^{238}\text{U}$. Measurements of three shards of glass from each the three concentration levels of the ~94% ^{235}U -enriched glasses (doped with NFRM U-1) also indicate that these glasses are not homogeneous within the precision of MC-ICP-MS. The isotopic relationship between the three concentration levels here is similar to that observed in the 53 % ^{235}U -enriched glasses, and the contaminant source is similarly suggested to be depleted in ^{235}U , relative to the NFRM U-1 dopant.

4c. Batch 3 Glass

This batch produced a SAC-Nat-500 glass, and was an attempt to produce a more homogeneous end product by reprocessing the SAC-Nat-500 glass from in Batch 2 through additional melting, mixing, and quenching steps. Both the re-ground SAC-NAT-500 powder was analyzed (3 samples), as well as shards from the re-fused glass (5 samples). Increased care was taken to minimize contamination from the furnace. Uranium concentration and isotopic composition results for the Batch 3 glass are given in Table 7.

Table 7: Uranium concentration and isotopic composition measurements of the Batch 3 glass. Isotope ratios are expressed as atom ratios, the standard uncertainty is given for (k=2).

Sample ID	U ($\mu\text{g/g}$)	uncert.	$^{235}\text{U} / ^{238}\text{U}$	uncert.	$^{234}\text{U} / ^{238}\text{U}$	uncert.	$^{236}\text{U} / ^{238}\text{U}$	uncert.
<i>CRM 112-A doped glass</i>								
<i>Powder, ~500 ppm</i>								
SAC-Nat-500 (1)	368.9	0.4	0.008179	0.000004	0.00006183	0.00000016	0.00000323	0.00000003
SAC-Nat-500 (2)	382.6	0.4	0.008185	0.000004	0.00006249	0.00000012	0.00000320	0.00000003
SAC-Nat-500 (3)	419.7	0.6	0.008188	0.000004	0.00006239	0.00000012	0.00000321	0.00000003
<i>Shards, ~500 ppm</i>								
SAC-Nat-500 (1)	254.2	0.3	0.008185	0.000004	0.00006240	0.00000012	0.00000332	0.00000003
SAC-Nat-500 (2)	251.1	0.4	0.008186	0.000004	0.00006228	0.00000012	0.00000335	0.00000003
SAC-Nat-500 (3)	278.8	0.4	0.008187	0.000004	0.00006227	0.00000012	0.00000333	0.00000003
SAC-Nat-500 (4)	246.2	0.4	0.008179	0.000004	0.00006218	0.00000012	0.00000330	0.00000003
SAC-Nat-500 (5)	257.8	0.4	0.008179	0.000004	0.00006210	0.00000012	0.00000329	0.00000003

The ground SAC-500-Nat starting material was reground powder from the fused SAC-Nat-500 glass (composition given in Table 6). The resultant U concentrations show that the heterogeneity in U is similar for the starting powder and the original, pre-powdered glass shards. The Concentration of uranium in the refused material, however, drops by nearly a factor of two (from 423 to 258 $\mu\text{g/g}$ on average, Table 4), suggesting volatile loss of uranium due to heating and re-fusing. Isotopic compositions of the powder and re-fused glass are identical in $^{235}\text{U}/^{238}\text{U}$, and similar in $^{234}\text{U}/^{238}\text{U}$, but the refused shards show distinctly elevated $^{236}\text{U}/^{238}\text{U}$ ratios relative to the powder, suggesting some ^{236}U contamination still manifested during the re-fusing process.

Five individual shards of the re-fused Batch 3 glass were selected for analysis. Despite additional effort of refusing these materials, the uranium concentrations from each measurement vary well outside of uncertainty, from 246.2 to 278.8 $\mu\text{g/g}$. The isotopic composition of the five measurements, however, overlaps within uncertainty for $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ (Fig. 5). The $^{234}\text{U}/^{238}\text{U}$ ratios did vary outside of uncertainty slightly (from 6.210×10^{-5} to 6.240×10^{-5}), but were far more similar than $^{234}\text{U}/^{238}\text{U}$ ratios in the previous Batches. Therefore, the additional steps taken to increase homogenization and decrease contamination to produce this glass were largely successful. This glass may be useful as a working reference material for spatially resolved techniques if some additional work is done to assess the magnitude of isotopic heterogeneity at the micro-scale.

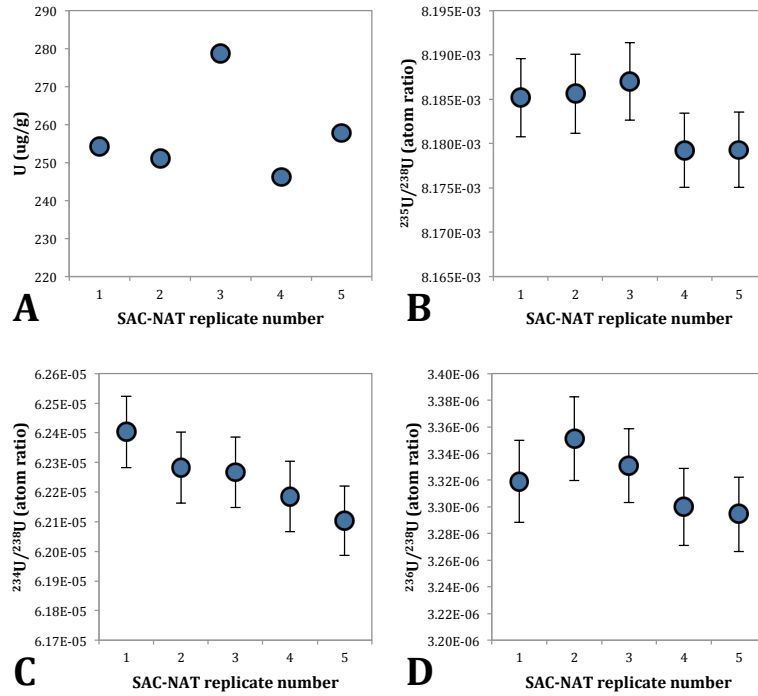


Figure 5: Uranium concentration (A) and isotopic composition (B, C, and D) of five replicate analyses from shards of the SAC-NAT-500 glass made in Batch 3. The standard uncertainty is shown for ($k=2$).

4d. Batch 4 Glasses

Glasses in this batch were an attempt to produce a more homogeneous end-product, using, as starting materials, samples produced in Batch 1. Similarly to Batch 3, the samples from Batch 1 were re-crushed and re-homogenized, with care taken to minimize the effects of furnace contamination. The results were largely successful, although uranium concentration homogeneity was again not achieved. For this effort we focused on the ~ 500 ppm uranium-doped glasses, as they were shown in Batch 1 to contain the least variability in isotopic composition. Uranium concentration and isotopic composition results from three shards of glass from each of the three Batch 4 glasses are given in Table 8.

As in the previous batches, the uranium concentrations of the three replicate measurements vary well outside of uncertainty for all three distinct isotopic compositions of glass. This precludes these samples from utility as uranium concentration working reference materials (Figs. 6A, 7A,

8A) where concentration measurements are needed to better than ~10%. The isotopic composition of the sample replicates, however, overlaps in most cases (Figs. 6-8), within the uncertainties of MC-ICP-MS measurements. For the CRM112-A doped uranium glass, the three measurements overlap in $^{234}\text{U}/^{238}\text{U}$. The $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios vary outside of uncertainty, although the RSD% of the $^{235}\text{U}/^{238}\text{U}$ ratio is only 0.24. The significant variation in $^{236}\text{U}/^{238}\text{U}$, while detectable by MC-ICP-MS measurements, is emphasized due to the low overall ^{236}U concentration.

Table 8: Uranium concentrations and isotopic compositions from measurement of the three Batch 4 glasses. Isotope ratios are expressed as atom ratios, the standard uncertainty is given for (k=2).

Sample ID	U (µg/g)	uncert.	$^{235}\text{U}/^{238}\text{U}$	uncert.	$^{234}\text{U}/^{238}\text{U}$	uncert.	$^{236}\text{U}/^{238}\text{U}$	uncert.
<i>CRM 112-A doped glass</i>								
CAS3-NAT-500 (1)	382.3	0.7	0.007929	0.000004	0.00006008	0.00000009	0.000002398	0.000000011
CAS3-NAT-500 (2)	367.9	0.6	0.007961	0.000004	0.00006015	0.00000008	0.000002502	0.000000012
CAS3-NAT-500 (3)	370.7	0.7	0.007964	0.000004	0.00006016	0.00000006	0.000002685	0.000000017
<i>NFRM U-2 doped glass</i>								
CAS3-53-500 (1)	340.9	0.3	1.1250	0.0006	0.010624	0.000008	0.007776	0.000003
CAS3-53-500 (2)	323.5	0.3	1.1255	0.0006	0.010622	0.000008	0.007775	0.000003
CAS3-53-500 (3)	330.0	0.3	1.1253	0.0006	0.010620	0.000008	0.007769	0.000003
<i>NFRM U-1 doped glass</i>								
CAS3-94-500 (1)	323.3	1.2	16.020	0.008	0.22477	0.00016	0.06979	0.00003
CAS3-94-500 (2)	351.6	1.4	16.063	0.008	0.22541	0.00017	0.06997	0.00004
CAS3-94-500 (3)	334.5	1.7	16.027	0.009	0.22505	0.00017	0.06980	0.00004

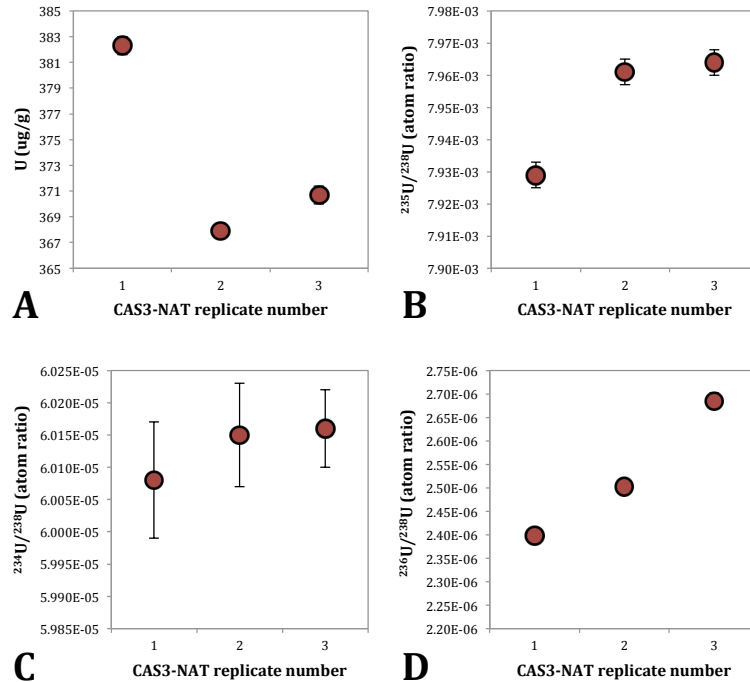


Figure 6: Uranium concentration (A) and isotopic composition (B, C, and D) of three analyses from shards of the CAS3-NAT-500 Batch 4 glass, doped with CRM112-A. The standard uncertainty is shown for (k=2).

The isotopic composition of the NFRM U-2 uranium-doped glass (~53% enriched in ^{235}U) is homogeneous within MC-ICP-MS measurement uncertainty for all three replicates (Fig. 7), making it the most homogeneous glass yet discussed. All three measured isotopic ratios are within uncertainty of each other for all three replicates. Uranium concentration, however, still varies well outside of uncertainty, and can only be considered homogenous to ~10%. The NFRM U-1 uranium-doped glass (~94% enriched in ^{235}U) shows variation in isotopic composition out of uncertainty for all three ratios, but the degree of variation is small, and the materials would be considered homogeneous for many isotopic measurement applications (Fig. 8). Calculated RSD% values for all three uranium isotope ratios are 0.14, well below the typical precision of spatially-resolved techniques. All three Batch 4 glasses may have utility for assessment of methods and instruments, where uranium isotope determinations are of interest, including application to spatially-resolved measurements, provided additional work is performed to assess heterogeneity at the micro-scale.

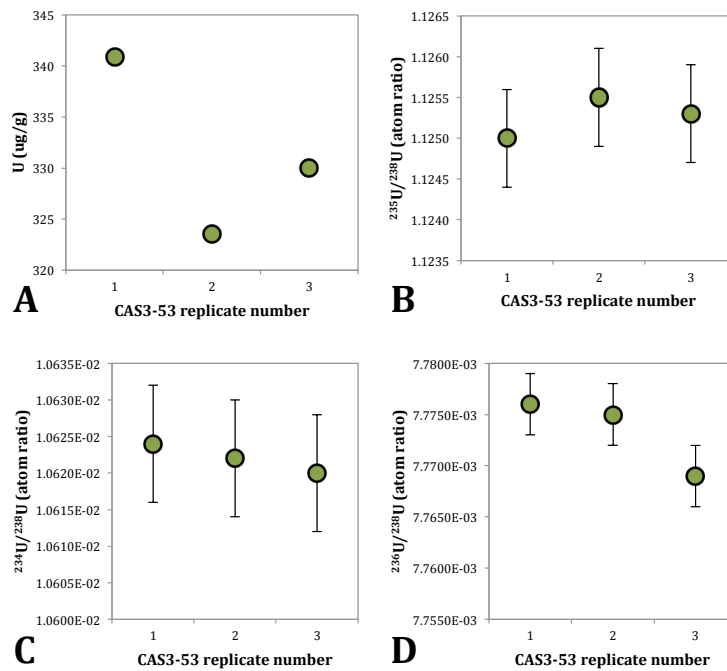


Figure 7: Uranium concentration (A) and isotopic composition (B, C, and D) of three analyses from shards of the CAS3-53-500 Batch 4 glass, doped with NFRM U-2. The standard uncertainty is shown for (k=2).

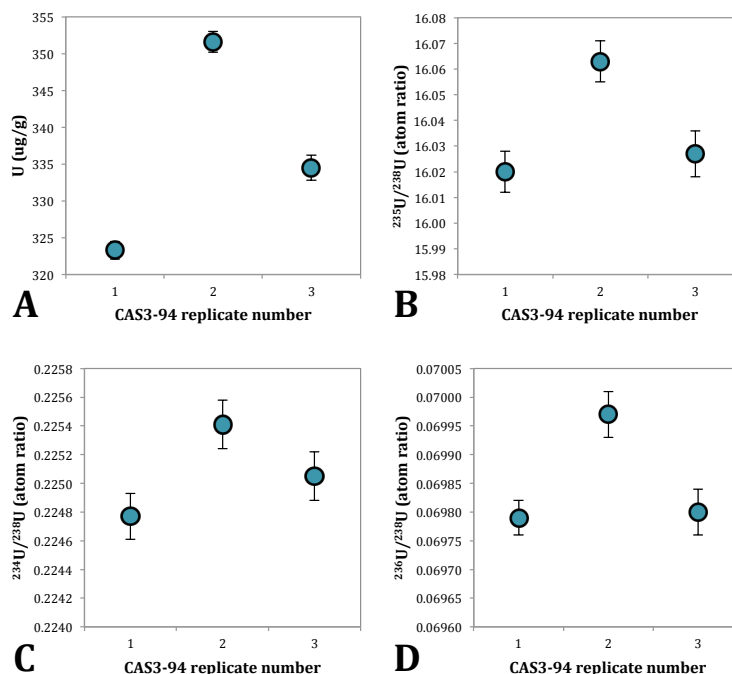


Figure 8: Uranium concentration (A) and isotopic composition (B, C, and D) of three analyses from shards of the CAS3-94-500 Batch 4 glass, doped with NFRM U-1. The standard uncertainty is shown for (k=2).

4e. Batch 5 Glasses

In Batch 5, a set of three glasses was produced using the ~53% ^{235}U enriched (NFRM U-2 doped) glasses in three concentrations. To produce a more homogeneous end-product, glasses produced in Batch 2 were re-processed, following the additional homogenization steps employed in Batch 3 and 4. Uranium concentration and isotopic composition results from analysis of three shards from each of the three Batch 5 glasses are given in Table 9.

Table 9: Uranium concentrations and isotopic compositions from measurement of the three Batch 5 glasses. Isotope ratios are expressed as atom ratios, the standard uncertainty is given for (k=2).

Sample ID	U ($\mu\text{g/g}$)	uncert.	$^{235}\text{U} / ^{238}\text{U}$	uncert.	$^{234}\text{U} / ^{238}\text{U}$	uncert.	$^{236}\text{U} / ^{238}\text{U}$	uncert.
<i>NFRM U-2 doped glass</i>								
<i>~5 ppm</i>								
SAC-53-5 (1)	4.38	0.06	0.9150	0.0005	0.006526	0.000005	0.004554	0.000002
SAC-53-5 (2)	4.30	0.09	0.9207	0.0005	0.006562	0.000005	0.004595	0.000002
SAC-53-5 (3)			0.9215	0.0005	0.006574	0.000005	0.004596	0.000002
<i>~50 ppm</i>								
SAC-53-50 (1)	38.5	0.8	1.0980	0.0006	0.007797	0.000005	0.005496	0.000003
SAC-53-50 (2)	42.7	0.5	1.0971	0.0006	0.007799	0.000006	0.005492	0.000002
SAC-53-50 (3)	44.4	0.6	1.1003	0.0006	0.007821	0.000005	0.005505	0.000002
<i>~500 ppm</i>								
SAC-53-500 (1)	434	3	1.1287	0.0006	0.008021	0.000006	0.005647	0.000002
SAC-53-500 (2)	414	7	1.1286	0.0006	0.008020	0.000006	0.005649	0.000002
SAC-53-500 (3)	392	6	1.1275	0.0006	0.008010	0.000006	0.005644	0.000002

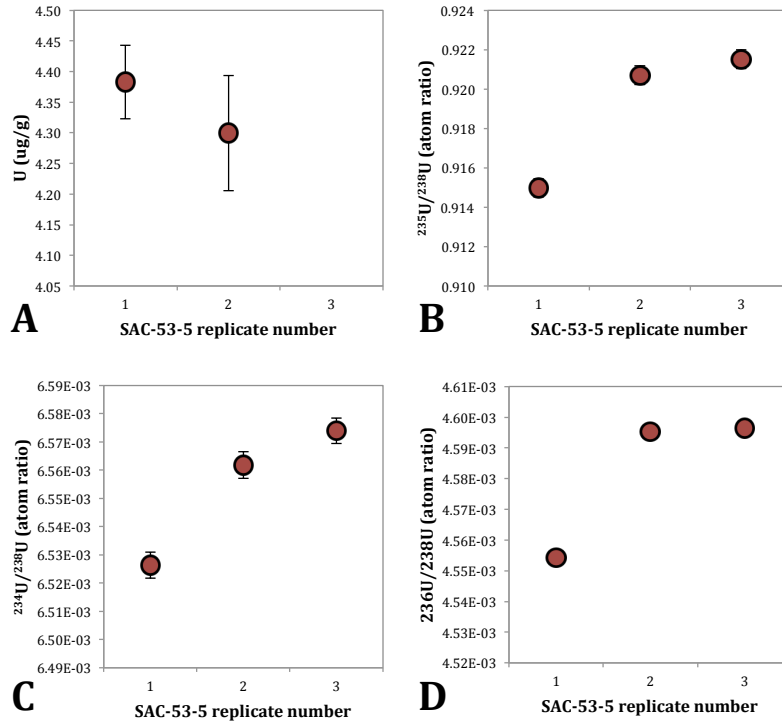


Figure 9: Uranium concentration (A) and isotopic composition (B, C, and D) of three analyses from shards of the SAC-53-5 Batch 5 glass, doped with NFRM U-2. The standard uncertainty is shown for ($k=2$). Uranium concentration was not measured in one sample.

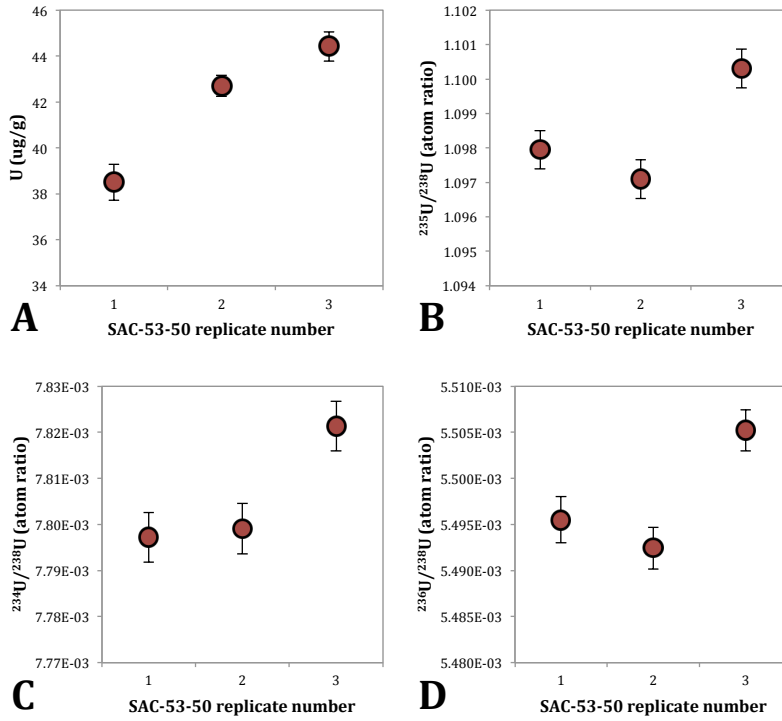


Figure 10: Uranium concentration (A) and isotopic composition (B, C, and D) of three analyses from shards of the SAC-53-50 Batch 5 glass, doped with NFRM U-2. Standard uncertainty is shown for ($k=2$).

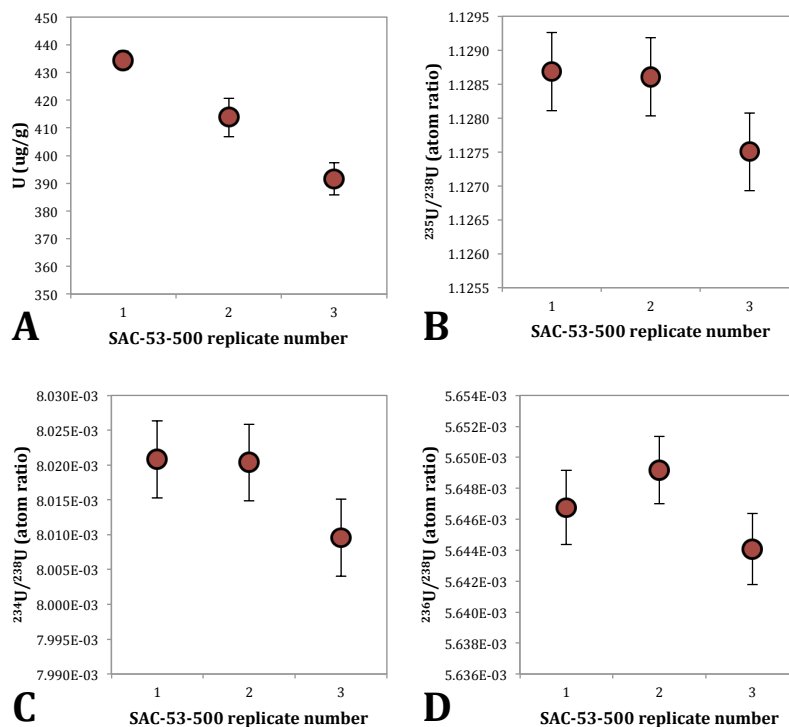


Figure 11: Uranium concentration (A) and isotopic composition (B, C, and D) of three analyses from shards of the SAC-53-500 Batch 5 glass, doped with NFRM U-2. Standard uncertainty is shown for ($k=2$).

Uranium concentration in the two of the three measured Batch 5 glasses showed minimal variation (Figs. 9A, 10A), but the uranium concentration in the most concentrated glass (SAC-53-500, Fig. 11A) continued to vary well outside of analytical uncertainty, demonstrating homogeneity of ~10%. For one of the three replicates on the lowest uranium concentration glass, a uranium concentration was not obtained. Therefore, we did not calculate the variance of only two replicates. Uranium isotopic composition results are unaffected by this.

Isotopic composition results vary outside of uncertainty for all measured uranium isotopic ratios of the lowest (~5 ppm) concentration glass (Fig. 9). Despite the lack of overlap, the RSD% of the $^{235}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$ of this standard are 0.39, 0.38, and 0.52, respectively, and may be sufficiently homogenous in isotopic composition for a variety of research applications.

The ~50 ppm glass replicates were more homogeneous than those of the ~5 ppm glass, although replicate #3 did not overlap in isotopic composition with the other two replicates (Fig. 10). However, the overall variation in isotopic composition between the replicates is again small, suggesting that this glass could be sufficiently homogenous in isotopic composition for a variety of research applications. The ~500 ppm glass analyses yielded overlapping isotope ratios for all uranium isotopes measured here, indicating relative homogeneity in terms of isotopic composition at the level of MC-ICP-MS methods. This glass is being considered for further spatial characterization, and may be useful for higher resolution uranium isotopic measurement techniques.

5. Recommendations and Conclusions

The 21 total glasses produced through this effort were not generated for use as analytical standards, and should not be used as such. All glasses measured here differ significantly from their expected U concentrations and isotopic compositions. However, as relative homogeneity was the primary goal and production of working reference materials for research and development applications needing low level uranium materials across a range of uranium concentrations and isotopic compositions, such deviations are not detrimental to the end product. Assessments of glass heterogeneity in uranium concentration and isotopic composition, however, reveal variable levels of heterogeneity, particularly in uranium concentration (generally no better than ~10%), and for some glasses, also in uranium isotopic composition. Thus, users of these glasses should consider the limits of homogeneity of these glasses prior to any research application.

5a. Uranium Concentration Considerations

With a few exceptions (noted in the text), the glasses produced in this study are not homogeneous in uranium concentration. Uranium concentration tended to vary significantly outside of measurement uncertainty, even for later batches where more homogeneous uranium isotopic compositions were achieved. Mechanisms applied in this study were unable to adequately mix the dopant uniformly into the glasses. Uranium loss by volatilization, while the glasses were molten, may also be a contributing factor. Thus, uranium concentrations reported here should be taken as “information” values. Any analyst utilizing these materials should not assume that any individual piece of glass taken from the bulk glass sample will contain the mean uranium concentrations reported here. Rather, the analyst should assume that uranium concentration can vary from 5-10 % on the macro-scale. Furthermore, uranium concentration might vary even more substantially on the micro-scale, and additional work should be performed to characterize micro-scale uranium concentration heterogeneity prior to application in spatial methods research.

5b. Uranium Isotopic Composition Considerations

The isotopic composition of the resultant glasses, particularly those of Batch 3, 4, and 5, are considerably more homogeneous than those of the initial manufacturing attempts (Batch 1 and 2). In some cases, all replicates overlapped within uncertainty for $^{235}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, and/or $^{236}\text{U}/^{238}\text{U}$. In two cases (B4-CAS-53-500 and B5-SAC-53-500), the replicate measurements of all three ratios overlapped within uncertainty. Although in most cases, isotopic heterogeneity was not achieved for all three ratios, measured isotopic ratios for standards in Batch 3, 4, and 5 may meet the requirements of many isotopic measurement research and development needs, which are in general less precise than the bulk analytical techniques employed here. It is possible, however, that uranium isotopic composition varies within single grains of glass, perhaps more widely than we can determine using a bulk measurement technique such as MC-ICP-MS. If select glasses are to be used in spatially-resolved applications, some additional work should be performed to characterize them, both on the macro-scale and the micro-scale.

5c. General Conclusions

These glasses were manufactured for the purposes of providing working materials useful for research and development applications, where low concentration uranium materials may be of

interest. Despite the clear demonstration of glass heterogeneity, these glasses may be considered useful materials for research and development purposes. MC-ICP-MS is an analytical technique with very high precision. Thus, while glass heterogeneity is measurable by MC-ICP-MS, the variation is still relatively small, particularly in terms of U isotopic composition.

Although we have sufficiently characterized the uranium concentration and isotopic composition of these glasses in bulk, it is important to note that we have made no effort to assess the possibility of micro-scale heterogeneity. We would expect observed heterogeneity to be greater on the micro-scale compared to the bulk scale utilized in this study, if present. However, it is equally important to note that micro-scale analytical techniques have much lower precision, on the whole, than the bulk analytical techniques used here. Laboratories utilizing these materials should consider performing additional characterization work to assess micro-scale heterogeneity prior to such application.

While the amounts of glass produced in this study are limited (gram quantities) it is the intention of this work to make these glasses available to the community by request, so far as possible. Interested parties can contact Kim Knight (knight29@llnl.gov), or Lawrence Livermore National Laboratory, directly.

6. References

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